CHAPTER 7

7. TWO- AND THREE-DIMENSIONAL CLUSTERS OF UREA AND THIOUREA

In this chapter we will consider two and three-dimensional hydrogen-bonding clusters of urea and thiourea. To analyze the trends, individual H-bonding components of the total stabilization energy are separated. The enthalpy of sublimation is estimated as the sum of these energies at the infinite size limit. The obtained value is in accord with the experimental data, as opposed to the value obtained in Chapter 4 from the dimeric interactions. We will conclude that the cooperative effects of H-bonding interactions dictate the crystal structures of urea and thiourea.

7.1 Geometry of the clusters and H-bond partition energy

We have considered partially optimized (under the constraints described above) herringbone arrangements for primary agglomerates (one-dimensional clusters) of two types: chains and ribbons (Figure 7.1). We will use the notations **C** for chain and **R** for ribbons followed by the number of monomers in this linear agglomerate. The number of the agglomerates in the cluster is specified after in the second digit. For example, a cluster of 3 ribbons, each built of 2 molecules will be denoted as **R2x3**. Stabilization energies $E_{n,m}$ as calculated for the urea and thiourea clusters at the AM1, HF/D95**, and B3PW91/D95** levels are presented in Table 7.1. In the case of ribbons the repeating unit has two molecules. Consequently, clusters consisting of ribbons one monomer long present a special case. Molecules in these clusters form
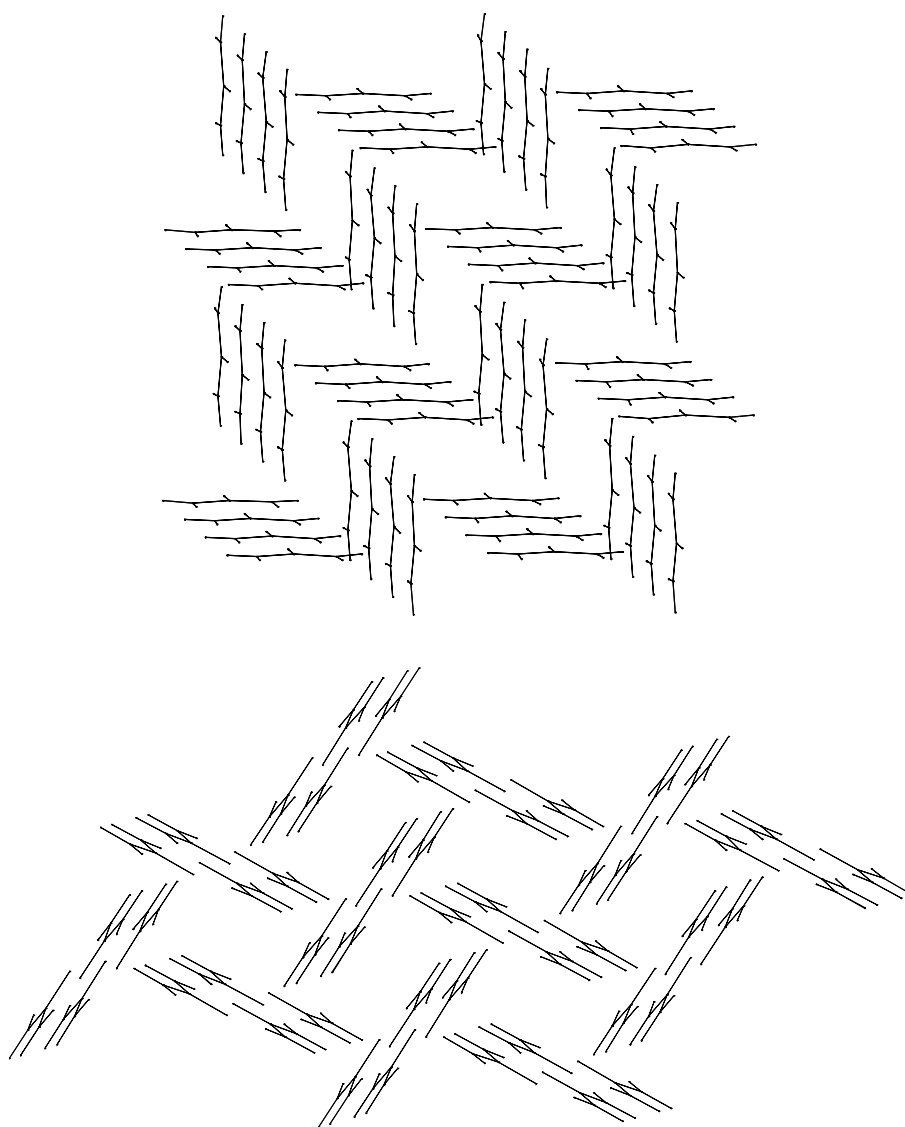
Figure 7.1. The cluster **C4x4x4**: chains of 4 monomers each, 4 chains in a layer, 4 layers in the structure (top), and **R4x4x3**: ribbons of 4 monomers each, 4 ribbons in a layer, 3 layers in the cluster (bottom).

H-bonds with only one of the two neighbors. Optimization of such a structure would lead to a collapse. Therefore, we performed a single-point calculation using the geometry optimized for clusters with two molecules in each ribbon. Moreover, for clusters with an even number of ribbons there are two isomers possible, each with a

Table 7.1. HF/D95**, DFT/D95**, and AM1 results on urea and thiourea clusters: enthalpy of interaction, kcal/mol

	CNx1	CNx2	CNx3	CNx4	CNx5	CNx6	CNx7	CNx8	RNx1	RNx2	RNx3	RNx4	RNx5	RNx6	RNx7	RNx8
										HF/D95**, urea						
									0.00	1.93	-2.38	-0.40	-5.01			
1	0.00	-4.19	-7.35	-11.10	-14.41	-18.14	-21.47	-25.19	0.00	-4.91	-2.38	-6.56	-5.01			
2	-6.90	-21.66	-34.08	-47.54	-60.50	-73.76			-9.51	-21.62	-33.86	-45.65	-57.98			
3	-16.00	-42.60	-65.55						-17.96	-43.27	-62.15					
4	-25.62	-63.75							-26.79	-59.30	-90.48					
5	-35.41	-84.80							-35.55	-80.39						
										B3PW91/D95**, urea						
1									0.00	2.65	-0.98	1.36				
1	0.00	-3.92	-6.33	-10.16	-13.20				0.00	-3.03	-0.98	-4.59				
2	-6.17	-19.97	-31.00	-43.37	-55.21				-10.91	-23.58	-36.42	-48.69				
3	-14.89	-40.18	-61.11						-20.85	-47.31	-68.01					
4	-24.32	-60.88							-31.14	-65.20						
5	-34.03	0.00							-41.43							
										AM1, urea						
1									0.0	1.3	-4.1	-2.5	-8.2	-6.5	-12.2	-10.5
1	0.0	-4.2	-7.7	-11.6	-15.2	-19.1	-22.8	-26.7	0.0	-4.6	-4.1	-8.6	-8.2	-12.6	-12.2	-16.7
2	-6.1	-21.2	-34.3	-48.5	-62.0	-76.1	-89.6	-103.7	-8.8	-21.2	-33.6	-45.6	-58.3	-70.3	-83.0	-94.9
3	-13.5	-39.9	-63.2	-88.2	-112.1	-136.9	-160.9	-185.7	-17.0	-41.9	-61.4	-85.9	-105.5	-130.0	-149.6	-174.1
4	-21.4	-58.9	-92.5	-128.4	-162.7	-198.3	-232.8	-268.4	-25.4	-57.9	-89.7	-121.3	-153.8	-185.3	-217.8	-249.3
5	-29.4	-77.9	-121.9	-168.7	-213.4	-259.9	-304.9	-351.2	-33.8	-78.6	-117.9	-162.2	-201.7	-246.0	-285.5	-329.8
6	-37.5	-97.0	-151.4	-209.0	-264.2	-321.5	-377.0	-434.2	-42.1	-94.2	-146.3	-197.6	-250.0	-301.3	-353.8	-405.0
7	-45.7	-116.1	-180.9	-249.4	-315.1	-383.2	-449.2	-517.2	-50.5	-115.3	-174.6	-238.6	-298.2	-362.2	-421.8	-485.8
8	-53.9	-135.2	-210.5	-289.7	-366.0	-444.9	-521.5	-600.2	-58.9	-130.9	-202.9	-274.0	-346.4	-417.5	-490.0	-561.0
										HF/D95**, thiourea						
1									0.00	1.68	-4.92	-2.97	-10.04			
1	0.00	-4.15	-7.53	-11.31	-14.82	-18.58	-22.30	-25.87	0.00	-5.18	-4.92	-10.17	-10.04			
2	-4.04	-17.13	-27.26	-37.93	-47.85				-7.32	-20.07	-33.38	-45.65	-59.13			
3	-9.68	-31.77	-49.67						-13.92	-39.48	-57.71					
4	-15.89	-47.17							-20.76	-51.56						
5	-22.34	-62.50							-27.53	-71.29						
										AM1, thiourea						
1									0.0	1.5	-2.6	-1.0	-5.5	-3.9	-8.4	-6.8
1	0.0	-4.2	-8.3	-11.8	-16.0	-19.5	-23.7	-27.3	0.0	-2.8	-2.6	-5.6	-5.5	-8.5	-8.4	-11.4
2	-4.3	-17.5	-29.2	-40.6	-52.8	-64.0	-76.3	-87.5	-9.7	-21.6	-33.9	-45.5	-57.9	-69.4	-81.8	-93.4
3	-10.3	-33.0	-52.8	-72.9	-93.6	-113.3	-134.3	-153.9	-19.1	-43.2	-63.4	-87.0	-107.3	-131.0	-151.3	-174.9
4	-17.0	-48.9	-77.1	-106.0	-135.3	-163.6	-193.2	-221.4	-28.8	-61.1	-93.8	-125.5	-158.4	-190.1	-223.0	-254.7
5	-23.9	-65.1	-101.6	-139.3	-177.2	-214.1	-252.5	-289.2	-38.4	-83.2	-124.0	-168.2	-209.1	-253.3	-294.2	-338.3
6	-31.1	-81.3	-126.2	-172.7	-219.2	-264.8	-311.9	-357.2	-48.2	-101.3	-154.6	-206.9	-260.4	-312.6	-366.2	-418.4
7	-38.3	-97.5	-151.0	-206.2	-261.3	-315.6	-371.3	-425.3	-57.9	-123.5	-185.0	-249.8	-311.5	-376.2	-437.9	-502.6
8	-45.6	-113.8	-175.8	-239.7	-303.5	-366.5	-430.8	-493.4	-67.6	-141.6	-215.6	-288.5	-362.8	-435.6	-510.0	-582.8

different number of H-bonds. For example, four ribbons of one monomer each could form two H-bonds (1-2 and 3-4) or one H-bond (2-3). That is why we report two sets of results for each **R1xN** cluster in Table 7.1.

In order for semi-empirical and *ab-initio* results to be comparable, we had to correct HF and DFT values for counterpoise (CP) and zero-point vibration energy (ZPVE). Unfortunately, full optimization, necessary to obtain ZPVE, significantly distorts most of the clusters considered here. Only single chains, ribbons, and chain trimers have the symmetry elements which guarantee the existence of a stationary point with planar molecules, similar to the clusters optimized under constraints. We performed HF/D95** frequency calculations for these clusters and estimated ZPVE for the other clusters based on the assumption of additivity.

The stabilization energies are interpreted in Table 7.2-7.3 in two ways. First, the energies of the last H-bond as chains (ribbons) grow, were obtained using the formula:

$$\Delta E_m = (E_{n,m} - E_{n,m-1} - E_{n,1})/n$$

where m represents the number of monomers in single chain (ribbon), and n the number of chains (ribbons) in the cluster. Second, the interaction energies between the cluster and the last chain (ribbon) added to it were obtained using the formula:

$$\Delta E_n = (E_{n,m} - E_{n-1,m} - E_{1,m})/h$$

where h is the number of H-bonds between the last chain (ribbon) and the rest of the cluster. In the case of chains, $h=n$; in the case of ribbons $h=[n/2]$.

7.2 The effect of cluster growth in two dimensions on enthalpy of interaction and individual H-bonds

As one can conclude from comparison of the left and right sides of Table 7.1, in the case of the thiourea the total stabilization energies of the ribbon clusters are lower than those of the chain clusters at any size. For urea, however, chain clusters

Table 7.2. HF/D95**, DFT/D95**, and AM1 results on urea clusters: enthalpy of the last H-bond within the chain (ribbon), and the last interchain (interribbon) interaction, kcal/mol

N	CNx1	CNx2	CNx3	CNx4	CNx5	CNx6	CNx7	CNx8	RNx1	RNx2	RNx3	RNx4	RNx5	RNx6	RNx7	RNx8
	HF/D95**, last H-bond in chain								HF/D95**, last H-bond in ribbon							
2	-6.90	-6.64	-6.46	-6.34	-6.34	-6.25			-9.51	-9.32	-9.70	-9.67	-9.59			
3	-9.11	-8.37	-8.04						-8.45	-8.37	-8.63					
4	-9.61	-8.48							-8.83	-8.98	-8.65					
5	-9.79	-8.43							-8.75	-8.09						
	B3PW91/D95**, last H-bond in chain								B3PW91/D95**, last H-bond in ribbon							
2	-6.17	-6.07	-6.11	-5.76	-5.76				-10.91	-11.60	-11.49	-11.37				
3	-8.72	-8.15	-7.93						-9.93	-10.35	-10.20					
4	-9.43	-8.39							-10.29	-10.27						
5	-9.72								-10.28							
	AM1, last H-bond in chain								AM1, last H-bond in ribbon							
2	-6.13	-6.45	-6.33	-6.33	-6.31	-6.30	-6.29	-6.29	-8.80	-8.97	-8.48	-8.63	-8.40	-8.52	-8.36	-8.47
3	-7.40	-7.27	-7.07	-7.02	-6.98	-6.95	-6.94	-6.92	-8.22	-8.03	-7.88	-7.93	-7.81	-7.85	-7.77	-7.81
4	-7.84	-7.41	-7.20	-7.13	-7.08	-7.04	-7.02	-7.00	-8.39	-8.62	-8.09	-8.21	-8.03	-8.13	-8.00	-8.08
5	-8.03	-7.45	-7.25	-7.17	-7.11	-7.07	-7.05	-7.02	-8.34	-8.04	-8.03	-8.08	-7.96	-8.01	-7.93	-7.98
6	-8.12	-7.46	-7.28	-7.18	-7.12	-7.08	-7.06	-7.03	-8.38	-8.45	-8.08	-8.22	-8.03	-8.13	-8.00	-8.08
7	-8.18	-7.47	-7.29	-7.19	-7.13	-7.09	-7.07	-7.04	-8.36	-8.26	-8.06	-8.11	-8.00	-8.05	-7.97	-8.01
8	-8.21	-7.47	-7.30	-7.19	-7.14	-7.09	-7.07	-7.05	-8.38	-8.47	-8.08	-8.23	-8.02	-8.13	-8.00	-8.09
	HF/D95**, chain-chain								HF/D95**, ribbon-ribbon							
1									1.93	-4.31	1.98	-4.61				
1		-4.19	-3.16	-3.75	-3.31	-3.73	-3.33	-3.72		-4.91	2.53	-4.18	1.56			
2		-3.93	-2.76	-3.28	-3.03					-2.59	-2.74	-2.28	-2.82			
3		-3.53	-2.31							-3.67	-0.46					
4		-3.13								-2.86	-2.19					
5		-2.80								-3.10						
	B3PW91/D95**, chain-chain								B3PW91/D95**, ribbon-ribbon							
1									2.65	-3.63	2.34					
1		-3.92	-2.41	-3.83	-3.04					-3.03	2.05	-3.61				
2		-3.81	-2.43	-3.10	-2.83					-1.75	-1.93	-1.36				
3		-3.47	-2.01							-2.81	0.08					
4		-3.06								-1.46						
	AM1, chain-chain								AM1, ribbon-ribbon							
1									1.31	-5.41	1.61	-5.66	1.66	-5.71	1.67	
1		-4.15	-3.52	-3.95	-3.60	-3.93	-3.61	-3.93		-4.62	0.52	-4.50	0.45	-4.49	0.44	-4.49
2		-4.47	-3.50	-4.04	-3.65	-4.00	-3.67	-3.99		-3.64	-3.58	-3.19	-3.87	-3.19	-3.88	-3.19
3		-4.27	-3.26	-3.84	-3.43	-3.78	-3.46	-3.77		-3.94	-1.22	-3.77	-1.26	-3.76	-1.27	-3.76
4		-4.03	-3.05	-3.64	-3.22	-3.58	-3.26	-3.56		-3.52	-3.24	-3.06	-3.54	-3.05	-3.56	-3.04
5		-3.82	-2.91	-3.48	-3.07	-3.42	-3.11	-3.40		-3.69	-1.87	-3.51	-1.93	-3.50	-1.93	-3.50
6		-3.66	-2.81	-3.35	-2.95	-3.29	-2.99	-3.28		-3.30	-3.33	-3.06	-3.43	-3.04	-3.45	-3.04
7		-3.53	-2.73	-3.25	-2.87	-3.20	-2.90	-3.18		-3.58	-2.20	-3.39	-2.26	-3.39	-2.27	-3.39
8		-3.42	-2.68	-3.17	-2.80	-3.12	-2.83	-3.10		-3.30	-3.28	-3.06	-3.38	-3.05	-3.40	-3.05

Table 7.3. HF/D95** and AM1 results on thiourea clusters: inctemental values for enthalpy of the last H-bond within the chain (ribbon), and the last interchain (interribbon) H-bond, kcal/mol

N	CNx1	CNx2	CNx3	CNx4	CNx5	CNx6	CNx7	CNx8	RNx1	RNx2	RNx3	RNx4	RNx5	RNx6	RNx7	RNx8
	HF/D95**, last H-bond in chain								HF/D95**, last H-bond in ribbon							
2	-4.04	-4.42	-4.06	-3.83	-3.64				-7.32	-8.28	-7.84	-8.13	-7.81			
3	-5.64	-5.24	-4.96						-6.60	-7.12	-6.47					
4	-6.21	-5.63							-6.84	-6.88						
5	-6.45	-5.59							-6.77	-7.28						
	AM1, last H-bond in chain								AM1, last H-bond in ribbon							
2	-4.32	-4.52	-4.21	-4.23	-4.16	-4.16	-4.12	-4.12	-9.72	-10.14	-9.58	-9.71	-9.38	-9.51	-9.28	-9.40
3	-5.99	-5.64	-5.13	-5.12	-4.97	-4.96	-4.89	-4.89	-9.38	-9.38	-8.96	-9.00	-8.79	-8.85	-8.72	-8.77
4	-6.66	-5.89	-5.34	-5.31	-5.13	-5.12	-5.03	-5.03	-9.69	-9.73	-9.28	-9.36	-9.12	-9.21	-9.04	-9.12
5	-6.97	-5.97	-5.42	-5.37	-5.18	-5.17	-5.07	-5.07	-9.65	-9.64	-9.22	-9.28	-9.05	-9.12	-8.97	-9.04
6	-7.14	-6.00	-5.47	-5.40	-5.20	-5.20	-5.09	-5.09	-9.72	-9.78	-9.31	-9.40	-9.15	-9.24	-9.08	-9.16
7	-7.24	-6.01	-5.49	-5.42	-5.22	-5.21	-5.10	-5.10	-9.71	-9.70	-9.29	-9.34	-9.12	-9.19	-9.04	-9.10
8	-7.30	-6.02	-5.51	-5.42	-5.23	-5.22	-5.11	-5.11	-9.74	-9.81	-9.33	-9.42	-9.16	-9.26	-9.09	-9.17
	HF/D95**, chain-chain								HF/D95**, ribbon-ribbon							
1									-5.18	0.26	-5.25	0.13				
1		-4.15	-3.39	-3.77	-3.51	-3.76	-3.71	-3.57	-5.42	-5.98	-4.95	-6.15				
2		-4.53	-3.04	-3.32	-2.94				-5.82	-4.31						
3		-4.14	-2.74						-5.02							
4		-3.85							-5.41							
	AM1, chain-chain								AM1, ribbon-ribbon							
1									1.50	-4.08	1.55	-4.46	1.62	-4.55	1.63	
1		-4.21	-4.05	-3.56	-4.19	-3.52	-4.21	-3.51	-2.82	0.23	-2.99	0.09	-2.98	0.04	-2.98	
2		-4.41	-3.69	-3.55	-3.95	-3.45	-4.00	-3.43	-2.16	-2.59	-1.84	-2.69	-1.82	-2.70	-1.82	
3		-4.12	-3.18	-3.26	-3.49	-3.12	-3.56	-3.09	-2.48	-0.55	-2.28	-0.59	-2.28	-0.60	-2.28	
4		-3.76	-2.79	-2.98	-3.10	-2.83	-3.17	-2.79	-1.78	-1.93	-1.48	-2.03	-1.45	-2.05	-1.45	
5		-3.44	-2.51	-2.75	-2.80	-2.60	-2.88	-2.55	-2.12	-0.79	-1.91	-0.83	-1.90	-0.83	-1.90	
6		-3.19	-2.31	-2.56	-2.58	-2.42	-2.66	-2.37	-1.66	-1.70	-1.38	-1.79	-1.35	-1.81	-1.35	
7		-2.99	-2.16	-2.41	-2.40	-2.28	-2.48	-2.23	-1.94	-0.91	-1.73	-0.95	-1.72	-0.96	-1.72	
8		-2.82	-2.05	-2.29	-2.27	-2.17	-2.34	-2.12	-1.60	-1.58	-1.33	-1.67	-1.31	-1.68	-1.30	

become more stable at size **3x3** at both HF and AM1 level.This result is in accord with the motif observed in crystal structure. By comparison, the linear clusters reported in Chapter 5 become more stable in chain structures starting with **C10** at HF, but not at AM1 level. To find a source for the stabilization of chain clusters we considered the energies of the different kinds of H-bonds separately. For this purpose we examined

the energy of the last H-bonds, as defined above, for clusters of different sizes. The results are reported in Tables 7.2-7.3 and in Figure 7.2.
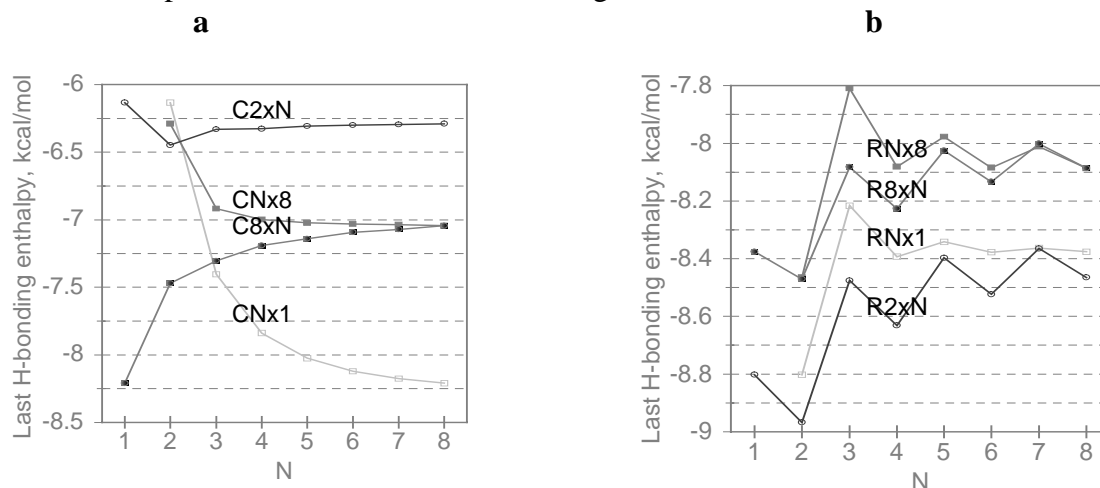

Figure 7.2. The last H-bond within the chains and ribbons for urea chain (a) and ribbon (b) clusters (AM1 results)

Examination of the Figure 7.2a shows that the last H-bond in chains becomes stronger as the chain grows (compare these values within the columns in Tables 7.2 and 7.3). However, in larger clusters this effect becomes much less pronounced (2% for **CNx8** vs. 11% for **CNx1** in the urea clusters and 4% vs. 21% respectively in the case of thiourea). From Figure 7.2b one may conclude that the last H-bond in ribbons, by contrast, becomes weaker as the ribbon grows. This effect also becomes less pronounced in larger clusters. For both chains and ribbons of the same length, the last H-bond becomes 5-10% weaker as the cluster grows in the other dimensions, increasing number of primary agglomerates in the cluster (compare the values within one row in Tables 7.2 and 7.3). As there are two molecules in the unit cell of a ribbon and two ribbons (chains) in the unit cell of a 2D cluster, this trend varies depending on whether the number of monomers in the cluster is even or odd.

The H-bonding interaction between chains of the same length (Figure 7.4)

follows trends similar to the ones observed within 1-D ribbons and transverse chains (see Section 5.6), with first H-bond being the most stable, second the least stable and converging to the intermediate limiting value. The H-bonds between the ribbons, however, seem to be converging to different values for even and odd numbers of ribbons in the cluster. The reasons for this phenomenon will be considered in the next Section. As chains and ribbons become longer, the H-bonds between them become considerably weaker, and convergence is not achieved at the size of eight monomers. To rationalize this counterintuitive trend, we will have to consider long-range electrostatic interactions.
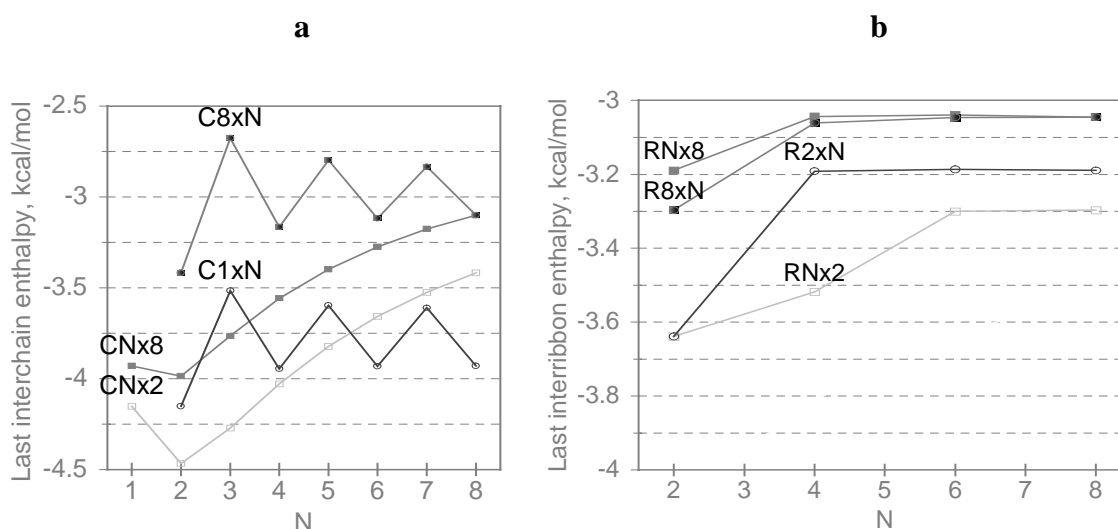
a   **b**

Figure 7.3. The last interchain (interribbon) interaction for urea chain (a) and ribbon (b) clusters (AM1 results).

Table 7.4. Incremental values for H-bonds in PC model (Mulliken HF/D95** point charges for monomer).

N	CNx1	CNx2	CNx3	CNx4	CNx5	CNx6	CNx7	CNx8	∞	RNx1	RNx2	RNx3	RNx4	RNx5	RNx6	RNx7	RNx8	∞
	last H-bond in chain									last H-bond in ribbon								
2	-4.85	-4.73	-4.59	-4.57	-4.53	-4.52	-4.50	-4.50	-4.41	-7.72	-7.68	-7.08	-7.25	-6.97	-7.11	-6.93	-7.04	-6.85
3	-5.61	-5.12	-4.91	-4.84	-4.78	-4.75	-4.73	-4.71	-4.62	-7.04	-6.56	-6.47	-6.43	-6.36	-6.35	-6.31	-6.31	-6.24
4	-5.84	-5.19	-4.97	-4.90	-4.83	-4.80	-4.77	-4.75	-4.64	-7.23	-7.26	-6.68	-6.83	-6.58	-6.70	-6.54	-6.64	-6.48
5	-5.95	-5.21	-5.00	-4.92	-4.85	-4.82	-4.79	-4.76	-4.65	-7.16	-6.67	-6.65	-6.58	-6.54	-6.52	-6.49	-6.48	-6.43
6	-6.00	-5.23	-5.02	-4.93	-4.86	-4.82	-4.79	-4.77	-4.66	-7.21	-7.31	-6.66	-6.85	-6.57	-6.71	-6.53	-6.65	-6.49
7	-6.02	-5.23	-5.03	-4.93	-4.90	-4.83	-4.80	-4.78	-4.67	-7.19	-6.68	-6.68	-6.61	-6.58	-6.55	-6.53	-6.52	-6.47
8	-6.06	-5.24	-5.04	-4.94	-4.92	-4.83	-4.80	-4.78	-4.68	-7.21	-7.34	-6.66	-6.86	-6.57	-6.72	-6.53	-6.65	-6.50
∞	-6.24	-5.42	-5.22	-5.12	-5.09	-4.96	-4.91	-4.88	-4.79	-7.18	-6.99	-6.65	-6.71	-6.55	-6.61	-6.51	-6.56	-6.48
	interchain H-bond									interribbon H-bond								
1										1.16	-4.98	1.37	-5.15	1.41	-5.19	1.42		-3.66
1		-4.00	-3.55	-3.57	-3.64	-3.55	-3.53	-3.66	-3.51	-4.31	0.50	-4.23	0.45	-4.22	0.44	-4.22		-3.66
2		-3.88	-3.28	-3.39	-3.40	-3.35	-3.31	-3.46	-3.33	-3.06	-2.64	-2.89	-2.85	-2.89	-2.88	-2.90		-2.79
3		-3.59	-2.99	-3.14	-3.12	-3.08	-3.04	-3.18	-3.04	-3.22	-0.70	-3.18	-0.72	-3.19	-0.74	-3.18		-2.55
4		-3.37	-2.80	-2.96	-2.92	-2.91	-2.86	-2.99	-2.85	-2.67	-2.32	-2.53	-2.48	-2.54	-2.50	-2.54		-2.45
5		-3.20	-2.68	-2.83	-2.79	-2.78	-2.73	-2.85	-2.71	-2.89	-1.19	-2.84	-1.24	-2.85	-1.25	-2.85		-2.40
6		-3.08	-2.59	-2.73	-2.69	-2.68	-2.63	-2.76	-2.61	-2.56	-2.24	-2.45	-2.36	-2.45	-2.38	-2.46		-2.37
7		-2.98	-2.53	-2.65	-2.65	-2.59	-2.56	-2.69	-2.54	-2.75	-1.43	-2.69	-1.48	-2.70	-1.48	-2.70		-2.35
8		-2.90	-2.48	-2.59	-2.62	-2.49	-2.50	-2.63	-2.48	-2.52	-2.21	-2.41	-2.32	-2.42	-2.33	-2.42		-2.34
∞		-2.71	-2.29	-2.41	-2.43	-2.32	-2.33	-2.46	-2.31	-2.37	-2.09	-2.30	-2.16	-2.30	-2.16	-2.31		-2.26

7.3 Point-charge model of interaction.

As discussed in Chapter 5 for ribbons, seemingly anticooperative behavior (weakening of H-bonds) could be attributed to the different number of the second neighbors (repulsive) interactions with respect to the number of the nearest neighbor (attractive) interactions. Likewise, the second neighbor interactions may be responsible for the anticooperative effects described in the previous Section. Due to the long range character of second neighbor interactions, one may expect electrostatic and polarization energy to be their major component. To examine the electrostatic component of H-bonding energy, we used a combination of atomic Mulliken point charges (PC) obtained in HF/D95** calculation of the urea monomer and the

geometry of AM1 optimized clusters. The results are presented in Table 7.4. As one can see, additive electrostatic energies follow general trends described above for the total energy of H-bonding interactions.

We used the geometry of the octamer to expand the cluster periodically in one and two dimensions and calculated the incremental value of H-bonds in the PC model. The value converged to 0.01 kcal/mol only after the molecules at 100Å from the central one were accounted for. The slow convergence of electrostatic energy is well known. These asymptotic limits for electrostatic interactions differ by about 0.2 kcal/mol from the values for the largest clusters considered here (**C8x8, R8x8**). The difference between these limits and the PC energy value a the finite size cluster can be used to correct ΔH values for all four types of H-bonds. The best estimated values for all methods are collected in Table 7.5.

Table 7.5. Best estimate for the enthalpy of H-bond formation and of sublimation. Dimeric values are shown for comparison.

	Urea			Thiourea	
	chains				
H-bond	AM1	HF/D95**	B3PW91/D95**	AM1	HF/D95**
Intrachain	-6.91	-8.75	-8.66	-5.11	-5.55
Interchain	-2.80	-3.38	-3.31	-2.12	-3.63
ΔHsub	-12.51	-15.51	-15.28	-9.35	-12.81
C2	-6.13	-6.85	-6.12	-4.32	-4.20
C1x2	-4.15	-4.46	-4.19	-4.21	-4.18
Sum of dimeric values	-10.28	-11.31	-10.31	-12.74	-12.56
Experiment	-21.	-21.	-21.		
	ribbons				
Intraribbon	-7.88	-10.23	-10.74	-9.17	-8.26
Interribbon	-2.88	-3.02	-1.62	-1.30	-5.19
ΔHsub	-10.76	-13.25	-12.36	-10.47	-13.45
C2	-8.80	-10.17	-11.57	-9.72	-7.78
C1x2	-4.62	-4.73	-2.85	-2.82	-5.15
Sum of dimeric values	-13.42	-14.90	-14.42	-12.54	-12.93
Experiment				-26.	-26.

Table 7.6. Total ΔH of interaction, and its components for urea 3D-clusters: AM1, PC and the difference (Δ).

	CNx4x4		Last H-bond within the chain				C4x4xN		Interchain H-bond		
N	AM1	PC	AM1	PC	Δ		AM1	PC	AM1	PC	Δ
1	-87.18	-84.29					-128.40	-101.73			
2	-275.90	-241.44	-6.35	-4.55	-1.79		-313.66	-256.54	-3.55	-3.32	-0.24
3	-474.05	-397.42	-6.94	-4.48	-2.46		-493.53	-407.31	-3.22	-3.07	-0.15
4	-674.59	-558.74	-7.08	-4.81	-2.27		-674.59	-558.74	-3.29	-3.11	-0.19
	RNx4x4		Last H-bond within the ribbon				R4x4xN		Interribon H-bond		
N	AM1	PC	AM1	PC	Δ		AM1	PC	AM1	PC	Δ
1	-54.46	-51.37					-121.27	-102.98			
2	-254.38	-202.53	-9.09	-6.24	-2.85		-284.61	-237.07	-2.63	-1.94	-0.69
3	-428.01	-349.73	-7.45	-5.99	-1.46		-448.91	-373.32	-2.69	-2.08	-0.61
4	-615.21	-504.93	-8.30	-6.49	-1.81		-615.21	-504.93	-2.81	-1.79	-1.02

7.4 Three-dimensional clusters

To evaluate the effect of the third dimension on H-bonding enthalpy we performed AM1 calculations for some 3D-clusters (Table 7.6). One can see that the last H-bond within both chains and ribbons displays oscillatory behavior, and for **4x4x4** clusters it is about 0.15 kcal/mol weaker than for corresponding 2D-clusters **4x4.** As in the case of 2D-clusters, the last H-bond becomes stronger for chains, and weaker for ribbons, as the chains (ribbons) grow. The interactions between primary agglomerates are also oscillatory and 0.15 weaker than in 2D-clusters. As 3D-clusters do not change the trends observed for 2D-clusters and are only available for clusters up to **4x4x4**, we will use values obtained for 2D-clusters to estimate the enthalpy of sublimation for urea and thiourea polymorphs.

7.5 Estimation of the enthalpy of crystal formation

The values collected in Table 7.5 for urea show that H-bonds within the primary agglomerates for chains are still weaker than for ribbons (in contrast to 1D-clusters). However, as the chains increase in size and in the number of H-bonds between them, they become more stable than ribbon structures. Yet H-bonds in thiourea chains are too weak for this to happen. H-bonding between primary agglomerates is stronger for ribbons of thiourea and for chains of urea. This is another factor in the distinction. The sublimation enthalpy comes to 15.5 kcal/mol. This far from the experimental value of 21 kcal/mol, but close to 3D-periodical HF result of 16.1 kcal/mol reported in Section 3.5.

Similar values, based on H-bonding enthalpy for the dimers, do not reproduce the experimentally found stability of the chain structure for urea or (in case of AM1) the experimentally found stability of the ribbon structure for thiourea. Hence, we can conclude that the cooperative effects of H-bonding interactions dictate crystal structures of these compounds.

7.6 Conclusions

We have reported the results of molecular and crystal orbital studies on hydrogen-bonded molecular crystals of urea and thiourea. Non-empirical quantum chemical methods were applied to compare the relative stability of polymorphic modifications. The periodical Hartree-Fock method, which underestimates dispersion energy, recovers about a half of the crystal sublimation enthalpy and reveals significant non-additive effects of hydrogen bonding in different directions. Cluster

calculations allow the study of individual components of the interaction energy due to the different kinds of H-bonds in these crystals. The extrapolated results of cluster calculations are in quantitative agreement with periodical results. Non-additive effects were found to be a reason for experimentally observed differences in crystal structures of urea and thiourea. Since these effects are not reproduced by standard empirical force fields, *ab initio* methods can be a useful tool in calculating the relative stability of different polymorphic modifications.

Even though it is probably not feasible to directly apply *ab initio* methods to predicting crystal structures in the nearest future, they may ultimately be an important part of the complex approach to this problem. The global search and initial selection of the candidates can be performed only using the empirical force fields. *Ab initio* methods can provide the qualitative understanding and quantitative data necessary to improve these force fields. Moreover, these methods may be used at the final step of the search, to reveal the most stable among possible crystal structures.

PUBLICATIONS

The results of this thesis were published (in part) in the following papers:

Sections 3.1, 3.2, 3.3: Cardenes-Jiron, G.I., Masunov, A., Dannenberg J.J: Molecular orbital study of crystalline *para*-benzoquinone. J. Phys. Chem. A; **1999**, 103(35); 7042-7046.

Sections 4.1, 4.4, 4.6: Masunov, A., Dannenberg, J.J.: Theoretical study of urea. I. Monomers and dimers J. Phys. Chem. A, **1999,** 103(1), 178 –184.

Section 4.6: Giribet, C.G.; Vizioli, C.V.; Ruiz de Azua, M.C.; Contreras, R.H.; Dannenberg, J.J.; Masunov, A., Proximity effects on nuclear spin-spin coupling constants, Part 2. The electric field effect on 1J(CH) couplings. J. Chem. Soc., Faraday Trans. **1996**, 92(17), 3029-3033.

Section 5.7: Dannenberg, J.J.; Haskamp,L.; Masunov, A. Are Hydrogen Bonds Covalent or Electrostatic? A Molecular Orbital Comparison of Molecules in Electric Fields and H-Bonding Environments, J. Phys. Chem. A; **1999**; 103(35); 7083-7086.

Sections 5.2,5.4,5.6: Masunov, A., Dannenberg, J.J.: Theoretical study of urea and thiourea. II. Higher oligomers J. Phys. Chem. B; **2000**, 104(4); 806-810.

Section 6.5: Masunov, A., Dannenberg, J.J. A theoretical investigation of the C-H...O interaction between substituted phenylacetylenes and water. J. Mol. Str. THEOCHEM **1996**, 371, 17-19.

Chapter 7: Masunov, A., Dannenberg, J.J.: Theoretical study of urea and thiourea. III. 2,3D-clusters. J. Phys. Chem. A; **2000**, to be submitted.